

Electrochromic Metallo-Supramolecular Polymer Nanosheets

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ABSTRACT

Blue and red colored metallo-supramolecular polymer nanosheets were successfully synthesized by the complexation of Fe(II) ion and ditopic or tritopic organic ligand at the liquid-liquid interface. The polymer films were insoluble in any solvent, but we could transfer the films on an ITO glass and revealed the excellent electrochromic properties.

1 INTRODUCTION

We reported electrochromic metallo-supramolecular polymer (MSPs) in 2007 for the first time [1] and revealed the electrochromic properties of Fe(II)-, Ru(II)-, and Co(II)-based MSPs [2,3]. Linear MSPs are synthesized by the complexation of metal ion and ditopic organic ligand (Fig. 1a). Nishihara et al. reported 2D nanosheets of MSPs using tritopic ligand (Fig. 1b) [4].

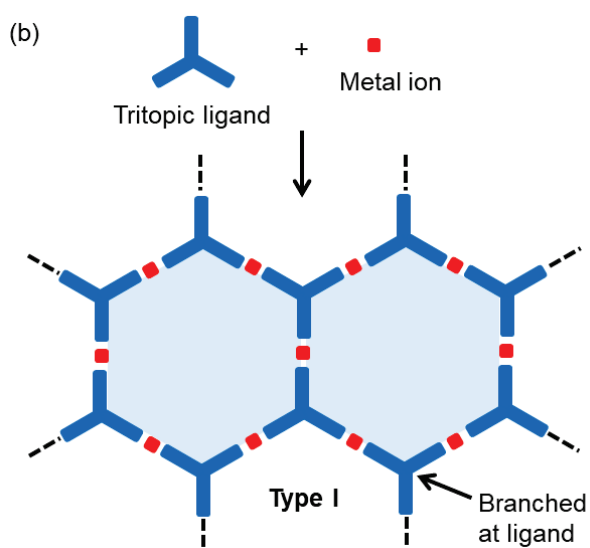
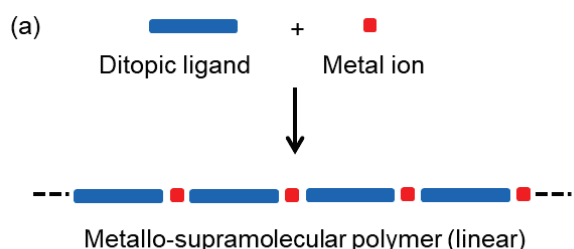


Fig. 1. Synthesis of (a) linear metallo-supramolecular polymer and (b) 2D nanosheets (Type I).

In this presentation I introduce new types of 2D nanosheet of MSPs by the combination of ditopic ligand bearing two bidentate coordination sites (Fig. 2a) and tritopic ligand bearing three bidentate coordination sites (Fig. 2b).

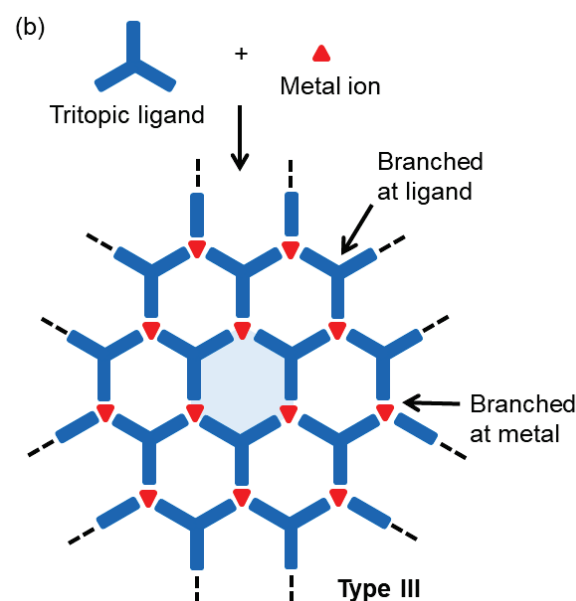
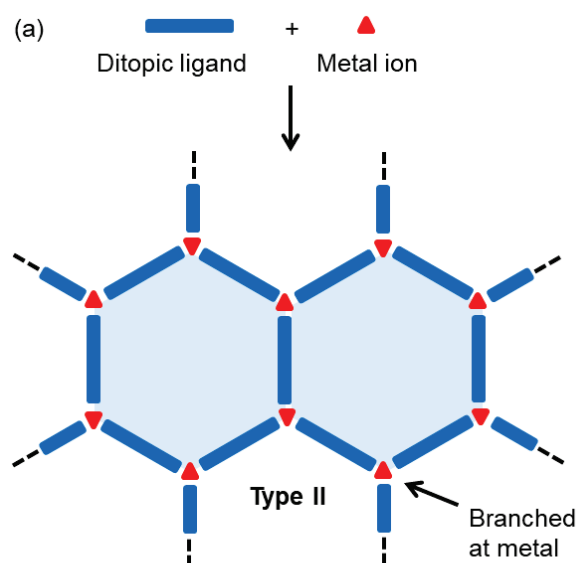


Fig. 2. Synthesis of 2D nanosheets of MSPs ((a) Type II and (b) Type III).

2 EXPERIMENT

In the synthesis of 2D nanosheets of MSPs, *trans*-1,2-bis(4'-methyl-[2,2'-bipyridin]-4-yl)ethene (**A**) and 1,4-bis(*trans*-2-(4'-methyl-[2,2'-bipyridin]-4-yl)vinyl)benzene (**B**) were used as ditopic ligands bearing two bidentate coordination sites [5] and 1,3,5-tris(1,10-phenanthroline)-benzene (**C**) was selected as tritopic ligand bearing three bidentate coordination sites (Fig. 3) [6].

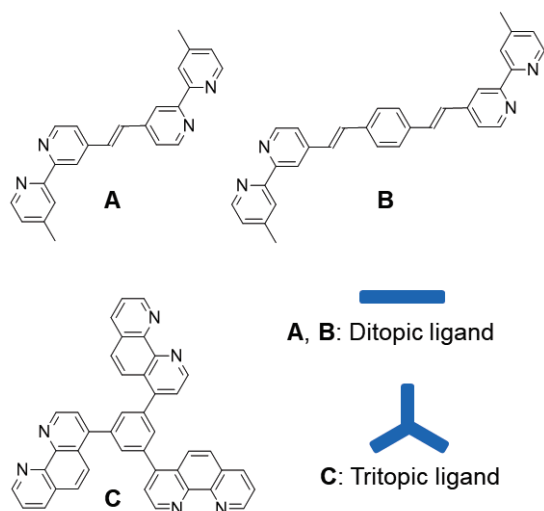


Fig. 3. Ditopic ligands bearing two bidentate coordination sites (**A**, **B**) and tritopic ligand bearing three bidentate coordination sites (**C**).

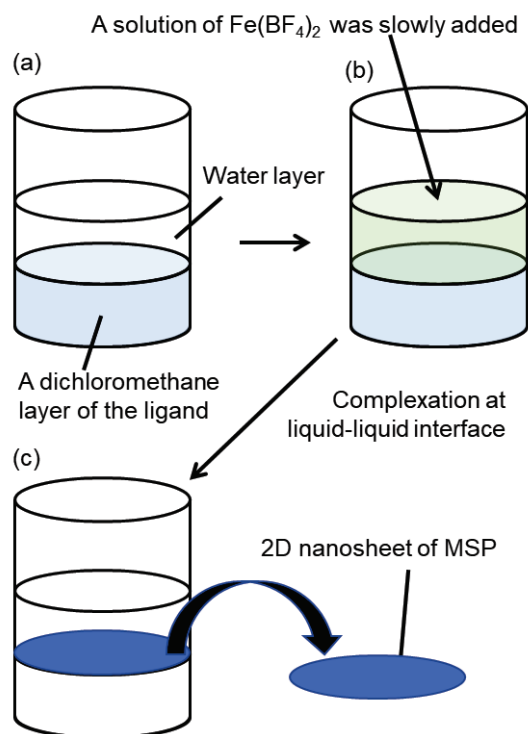


Fig. 4. (a-c) Synthetic procedure of 2D nanosheets of MSP.

$\text{Fe}(\text{BF}_4)_2$ was used as metal salt. A dichloromethane layer of the ligand and a water layer were prepared in a beaker (Fig. 4a). Then, a water solution of $\text{Fe}(\text{BF}_4)_2$ was slowly added to the water layer (Fig. 4b). Gradually, a colored film of 2D nanosheets of MSP was formed at the liquid-liquid interface, by the complexation of the ligand and the metal ion.

The prepared film was transferred on an ITO glass to investigate the EC properties. In addition, EC devices with the polymer nanosheets were fabricated.

3 RESULTS AND DISCUSSION

3.1 Synthesis of 2D Nanosheets

The 2D nanosheets of MSPs (polyFe-A, -B, -C) were synthesized by the complexation of $\text{Fe}(\text{II})$ ions and the ligand **A**, **B**, or **C** at a liquid-liquid interface between a water layer of the metal salt and a dichloromethane layer of the ligand at room temperature. The polymer formation was confirmed by the color change because the metal complex moieties of the polymer have metal-to-ligand charge transfer (MLCT) absorption. Interestingly, the color is different among the polymers. The color of polyFe-A, -B, and -C was blue, magenta, and red, respectively. The maximum wavelength of the MLCT absorption, observed in the UV-vis spectra of the nanosheets, were 590, 568, and 518 nm, respectively. These wavelengths are close to that of $\text{Fe}(\text{II})$ -based MSP composed of $\text{Fe}(\text{II})$ ion and bis(terpyridyl)benzene [2]. $\text{Fe}(\text{II})$ ion has an octahedral coordination geometry with six coordination sites. Therefore, the 2,2'-bipyridine or 1,10-phenanthroline moiety of the ligands **A**, **B**, and **C** is complexed with $\text{Fe}(\text{II})$ at the 3:1 molar ratio (Fig. 5). According to the branched structures in the metal complexes, polyFe-A, -B, and C are expected to form Type II, II, and III of nanosheet structures, respectively (Fig. 2). The thickness of the polymer film was increased by enhancing the reaction time.

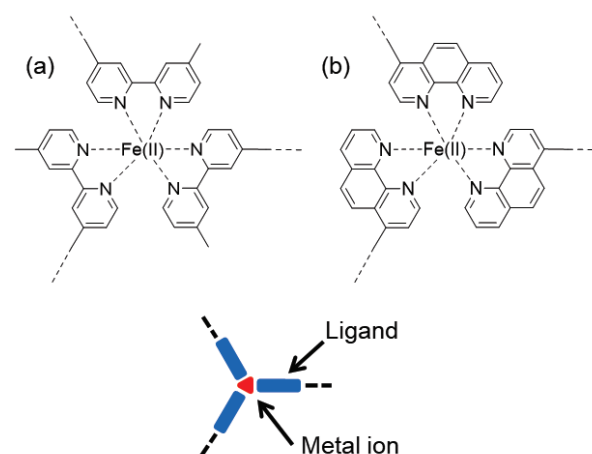


Fig. 5. The complex moieties of 2D nanosheets: (a) polyFe-A and -B and (b) polyFe-C.

3.2 EC Properties

The nanosheets were obtained as insoluble films. So, the films were directly transferred on an ITO glass to investigate the electrochemical and EC properties. The redox potentials ($E_{1/2}$) of Fe(II)/(III) in polyFe-A, -B, and -C were determined by cyclic voltammetry to be 0.68, 0.61 and 0.75 V vs Ag/Ag⁺, respectively. The three polymer films showed reversible EC changes between the more and less oxidative potentials than the redox potential of Fe ion. These results suggest the EC changes are triggered by the redox of Fe(II) ion. In polyFe-A, the color change between blue and colorless was observed. PolyFe-C also showed the color change to colorless by applying the oxidative potential. On the other hand, the color change in polyFe-B was from magenta to yellow. The yellow color in the oxidized state is considered to come from the color of the π -conjugated ligand **B**.

The response time to change the color (applied potentials: 1 V or 0 V vs Ag/Ag⁺) was very fast. It was 0.48 sec for coloring and 0.57 sec for bleaching in polyFe-A. The response in polyFe-B was also fast (0.50 sec for coloring and 0.54 sec for bleaching). On the other hand, the response time in polyFe-C was 3.3 sec for bleaching and 2.9 sec for coloring, which were longer than those of polyFe-A and polyFe-B. These results indicate that the anion transfer penetrating the nanosheets during the redox of Fe ions is not so fast in polyFe-C because of the dense hexagonal structure of the nanosheet.

The maximum difference in transmittance between the colored and colorless states of polyFe-A, -B, and -C was 62, 57, and 55 %, respectively. Coloration efficiency of polyFe-A, -B, and -C was 431, 382, and 230 cm²/C, respectively.

3.3 EC Devices

One of the advantages on the EC device using the nanosheets is the easy processability. In the case of linear metallo-supramolecular polymer, spray coating of the polymer solution on an ITO glass is necessary.

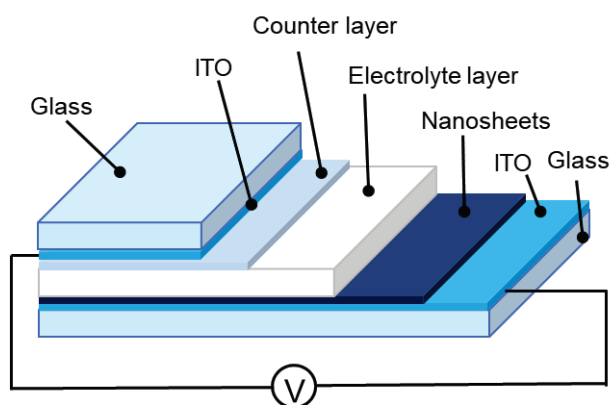


Fig. 6. A structure of an EC device using the polymer nanosheets.

On the other hand, coating of the polymer nanosheets on an ITO glass was finished by the simple transfer of the polymer film. EC devices shown in Fig. 6 were fabricated using the nanosheets. Since the polymer film was robust and insoluble in the electrolyte layer, the EC devices showed high durability for the repeated color changes. Especially, an EC device with polyFe-C, which had a highly dense hexagonal Type III structure, showed stable color changes more than 15,000 cycles.

4 CONCLUSIONS

It was revealed that the combination of ditopic or tritopic ligands bearing two or three bidentate coordination sites and Fe(II) ions having six coordination sites was suitable to synthesize 2D nanosheets of MSPs by their complexation at a liquid-liquid interface. The polymer films showed excellent EC properties. EC devices with the polymers were also nicely fabricated and exhibited high durability for the repeated EC changes.

ACKNOWLEDEMENT

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